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SAKAMOTO HIROYUKI**(54) CATIONIC ELECTRODEPOSITION COATING COMPOSITION, METHOD FOR FORMING FILM AND COATED PRODUCT HAVING FILM**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a new cationic electrodeposition coating composition using a resin composition having sulfonium groups and propargyl groups and carrying out film curing by photopolymerization after the coating, to provide a method for forming the film and to thereby realize low-temperature curing and short-time curing.

**SOLUTION:** This cationic electrodeposition coating composition is characterized as comprising the resin composition having the sulfonium groups and propargyl groups and a photopolymerization initiator.

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**CLAIMS**

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[Claim(s)]

[Claim 1] A resin constituent with a sulfonium radical and a propargyl radical, and the cation electrodeposition paint constituent characterized by including a photopolymerization initiator.

[Claim 2] A photopolymerization initiator is a cation electrodeposition paint constituent according to claim 1 which is 0.2 - 8 % of the weight to the resin solid content weight in a cation electrodeposition paint constituent.

[Claim 3] The resin constituent with a sulfonium radical and a propargyl radical is a cation electrodeposition paint constituent according to claim 1 or 2 whose sum total content of a sulfonium radical and a propargyl radical 10-495mmol content of 5 - 400mmol and the propargyl radical is carried out per 100g of resin solid content in a cation electrodeposition paint constituent, and for a sulfonium radical, and is 500 or less mmols.

[Claim 4] The resin constituent with a sulfonium radical and a propargyl radical is a cation electrodeposition paint constituent according to claim 1, 2, or 3 whose sum total content of a sulfonium radical and a propargyl radical it consists of resin which makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, and has 700-5000 as number average molecular weight, 20-395mmol content of 5 - 250mmol and the propargyl radical is carried out per 100g of solid content of said resin constituent, and for a sulfonium radical, and is 400 or less mmols.

[Claim 5] The paint film formation approach which carries out electropainting of the cation electrodeposition paint constituent according to claim 1, 2, 3, or 4 to a coated object, and is characterized by including the process which irradiates ultraviolet rays at the coat obtained.

[Claim 6] Furthermore, the paint film formation approach including the process which heats the coat obtained according to claim 5.

[Claim 7] All or a part of time amount which performs UV irradiation is the paint film formation approach according to claim 6 which is what heats to coincidence.

[Claim 8] The coated object characterized by having the paint film obtained by the paint film formation approach according to claim 5, 6, or 7.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the coated object which has the paint film obtained in more detail by the paint film formation approach and it using the cation electrodeposition paint constituent, in which hardening by ultraviolet rays is possible, and this about the coated object which has the paint film obtained by the paint film formation approach and it which uses a cation electrodeposition paint constituent and this.

[0002]

[Description of the Prior Art] Generally, the painting process of an automobile etc. consists of carrying out heat hardening of an intermediate coat and the paint film which top coat is subsequently painted and is obtained, after carrying out the under coat paint by the cation electrodeposition paint to the coated object to which chemical conversion was beforehand performed by phosphate etc.

[0003] Among these, cation electroplating performed as under coat paint is performed considering corrosion prevention, rust proofing, etc. as a key objective, and the cation electroplating paint containing a resin constituent with a sulfonium radical and a propargyl radical is indicated by JP.2000-38525A. The cation electroplating paint containing a resin constituent with this sulfonium radical and a propargyl radical is excellent in hardenability and throwing power of electrolytic coloring.

[0004] On the other hand, conventionally, since the configuration is complicated, as for photocuring, light is not usually used for the electroplating approach applied to the car body and components of an automobile in homogeneity.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention offers the new cation electroplating paint constituent and the paint film formation approach of making photopolymerization perform paint film hardening after cation electroplating using the resin constituent which has a sulfonium radical and a propargyl radical as paint film plasticity resin, and is for this to realize acid cure and short-time hardening.

[0006]

[Means for Solving the Problem] When this invention person includes a photopolymerization initiator in the cation electroplating paint constituent containing a resin constituent with a sulfonium radical and a propargyl radical (when performing the optical exposure of UV irradiation etc. on the electroplated coat obtained by cation electroplating) A header and this invention were completed for hardening of an electroplated coat progressing by the sulfonium radical contained in an electroplated coat generating a radical in response to an optical exposure, and this radical acting on an allyl association generated with the electroplated coat, and making a polymerization perform.

[0007] That is, this invention is a resin constituent with a sulfonium radical and a propargyl radical, and a cation electroplating paint constituent characterized by including a photopolymerization initiator. As for the above-mentioned photopolymerization initiator, it is desirable that it is 0.2 ~ 5 % of the weight to the resin solid content weight in the above-

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sulfonium radical and a propargyl radical in above-mentioned semantics.

[0014] The above-mentioned sulfonium radical is a hydration functional group of the above-mentioned resin constituent. On an electrode, an ionic radical can disappear in response to an electrolytic reduction reaction, and a sulfonium radical can be irreversibly nonconductorized. If the electrical potential difference or current more than fixed can be given in an electroplating process, it is thought that the cation electroplating paint constituent of this invention can demonstrate advanced throwing power of electrolytic coloring by this.

[0015] In the electroplating process in which the cation electroplating paint constituent of this invention is used, electrode reaction is triggered, and when a sulfonium radical holds the produced hydrosulfide ion, an electrolysis generating base is considered to generate in an electroplated coat. This electrolysis generating base can change into reactive high allyl association by having the resonant low propargyl radical by heating which exists in an electroplated coat.

[0016] Especially as resin used as the frame of the resin constituent contained in the cation electroplating paint constituent of this invention, although not limited, an epoxy resin is used suitably. Poly glycidyl ether of the thing acrylate ester polybutadiene; novolac phenol mold Port epoxy resin; novolac cresol mold Port epoxy resin; poly glycidyl acrylate; aliphatic series polyol which specifically [as an epoxy resin, what has at least two or more epoxy groups is suitably used into 1 molecule, and] carried out chain extension of an EPIBSU epoxy resin and this by diol, dicarboxylic acid, diamine, etc., or polyether polyol the Port epoxy resins, such as poly glycidyl ether of a polybiscyclic carboxylic acid, can be mentioned. Since the formation of a polyfunctional radical for raising hardenability is [among these] easy, a novolac phenol mold Port epoxy resin, a novolac cresol mold Port epoxy resin, and poly glycidyl acrylate are desirable. In addition, some above-mentioned epoxy resins may be mono-epoxy resins.

[0017] The resin constituent contained in the cation electroplating paint constituent of this invention consists of resin which makes the above-mentioned epoxy resin a frame, and number average molecular weight is 500~20000. The casting efficiency of cation electroplating worsens that number average molecular weight is less than 500, and if 20000 is exceeded, a good coat cannot be formed on a coated object front face. When more desirable molecular weight can be set up according to a resin frame, for example, it makes a novolac phenol mold epoxy resin or a novolac cresol mold epoxy resin into a frame, as for the above-mentioned number average molecular weight, it is more desirable that it is 700~5000.

[0018] The contents of the sulfonium radical in the resin constituent in the cation electroplating paint constituent of this invention are per [5] 100g of resin solid content in the above-mentioned cation electroplating paint constituent ~ 40mmol, after fulfilling the conditions of the content of the sulfonium radical mentioned later and a propargyl radical.

Sufficient throwing power of electrolytic coloring or hardenability cannot be demonstrated as they are 5mmol(A) / less than 100g, and hydration and both stability worsen. If it exceeds 40mmol(A) / 100g, a deposit of the coat on the front face of a coated object will worsen. When considering of resin with which a more desirable content can be set up according to the resin frame used, for example, the above-mentioned resin constituent makes a frame a novolac phenol mold epoxy resin or a novolac cresol mold epoxy resin, as for the content of the above-mentioned sulfonium radical, it is more desirable that they are per [5] 100g of resin solid content in the cation electroplating paint constituent of this invention ~ 25mmol, and its 10 ~ 15mmol is still more desirable.

[0019] In the above-mentioned cation electroplating paint, although the reason of the propargyl radical in the resin constituent in the cation electroplating paint constituent of this invention is unknown, it not only acts as a hardening functional group, but it can raise further the throwing power of electrolytic coloring of the above-mentioned cation electroplating paint constituent by reacting with a sulfonium radical.

[0020] The contents of the propargyl radical in the resin constituent in the cation electroplating paint constituent of this invention are per [10] 100g of resin solid content in the above-mentioned cation electroplating paint constituent ~ 495mmol, after fulfilling the conditions of the content of the sulfonium radical mentioned later and a propargyl radical. When

mentioned cation electroplating paint constituent. The resin constituent with the above-mentioned sulfonium radical and a propargyl radical carries out 10~495mmol content of 5 ~ 40mmol and the propargyl radical per 100g of resin solid content in the above-mentioned cation electroplating paint constituent, and for a sulfonium radical, and it is desirable that the sum total content of a sulfonium radical and a propargyl radical is 500 or less mmols. The resin constituent with the above-mentioned sulfonium radical and a propargyl radical consists of resin which makes a frame a novolac phenol mold epoxy resin or a novolac cresol mold epoxy resin again, has 700~5000 as number average molecular weight, and carries out 20~395mmol content of 5 ~ 25mmol and the propargyl radical per 100g of resin solid content of the above-mentioned resin constituent, and for a sulfonium radical, and it is desirable that the sum total content of a sulfonium radical and a propargyl radical is 400 or less mmols.

[0021] This invention is the cation electroplating approach which carries out electroplating of the above-mentioned cation electroplating paint constituent to a coated object, and is characterized by including the process which irradiates ultraviolet rays at the coat obtained again. As for the above-mentioned cation electroplating approach, it is desirable that it is a time including the process which heats the coat obtained further, and, as for all or a part of time amount which performs the above-mentioned UV irradiation, it is more desirable that it is what heats to coincidence. This invention is a coated object characterized by having further the coat obtained by the above-mentioned cation electroplating approach. Hereafter, this invention is explained in a detail.

[0022] The cation electroplating paint constituent of cation electroplating paint constituent this invention contains a photopolymerization initiator. It is not limited especially as the above-mentioned photopolymerization initiator. For example, a benzoin, benzoin isopropyl ether, Benzoin, such as benzoin isobutyl ether; A benzophenone, Benzophenone, such as a 4 and 4'-screw (dimethylamino) benzophenone (DMHRAZU (Kanto)), Xanthone, Xanthone, such as a thioxanthone; A 2-phenyl-2-hydroxyacetophenone, An alpha and alpha-dichloro-4-phenoxycarboxyphenone, 1-hydroxy cyclohexyl-phenyl ketone, 2 and 2-diethoxy acetophenone, 2-hydroxy-2-methyl-1-phenylpropane-1-one, Acetophenone, such as a 2-hydroxy-2-methyl-2-methyl-2-phenylacetophenone, 2 and 2-dimethoxy-2-phenylacetophenone (benzyl dimethyl ketal) in addition to this 4-dimethylamino ethyl benzoate, 4, 4'-diiodo still benzene -2, a 2'-diphenyl acid, the 1-phenyl -1, a 2-propene dione-2-(4-ethoxybenzoyl) oxime, etc. can be mentioned. Especially, benzyl dimethyl ketal is desirable. One sort or two sorts or more can be used for these. The above-mentioned photopolymerization initiator can be prepared by the well-known approach, for example, a commercial item can also be used for it.

[0023] As for the above-mentioned photopolymerization initiator, it is desirable that it is 0.2 ~ 5 % of the weight to the resin solid content weight in the cation electroplating paint constituent of this invention. If photopolymerization may become inadequate when it is less than 0.2 % of the weight, and it exceeds 5 % of the weight, it is easy to produce unevenness in extent of hardening, and may be inferior to paint film physical properties. Preferably, it is 1 ~ 5 % of the weight.

[0024] The cation electroplating paint constituent of this invention contains a resin constituent with a sulfonium radical and a propargyl radical further. After painting an intermediate coat on the electroplated paint film which is not hardened (which the throwing power of electrolytic coloring in which the cation electroplating paint constituent of this invention was excellent in cation electroplating is obtained by including such a resin constituent, and is obtained especially), both the shape hardening paint film obtained can be used suitable also for the double layer paint film formation approach heated to coincidence.

[0025] Although the resin which constitutes the above-mentioned resin constituent may have both sulfonium radical and propargyl radical in the mixed, the need does not exist, for example, may not necessarily have either the sulfonium radical or the propargyl radical in the mixed. In the case of this latter, it has these two sorts of all hardenability functional groups at the whole resin constituent. That is, the above-mentioned resin constituent may consist of mixture of resin only with the resin and the propargyl radical which consist of resin with a sulfonium radical and a propargyl radical, or have only a sulfonium radical, or may consist of all these mixture. The resin constituent contained in the cation electroplating paint constituent of this invention has a

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sufficient throwing power of electrolytic coloring or hardenability cannot be demonstrated as they are 10mmol(A) / less than 100g, but it exceeds 495mmol / 100g, there is a possibility of having a bad influence on the hydration stability at the time of using it as a cation electroplating paint. When considering of resin with which a more desirable content can be set up according to the resin frame used, for example, the above-mentioned resin constituent makes a frame a novolac phenol mold epoxy resin or a novolac cresol mold epoxy resin, as for the content of the above-mentioned propargyl radical, it is more desirable that they are per [20] 100g of resin solid content in the cation electroplating paint constituent of this invention ~ 295mmol.

[0026] Moreover, the sum total content of the sulfonium radical in the resin constituent contained in the cation electroplating paint constituent of this invention and a propargyl radical is 500 or less mmols per 100g of resin solid content in the above-mentioned cation electroplating paint constituent. If 500mmol(A) is exceeded, resin may not be obtained in fact or the target engine performance may not be obtained. The sum total content of the sulfonium radical in the above-mentioned resin constituent and a propargyl radical can set up a more desirable content according to the resin frame used, for example, in the case of a novolac phenol mold epoxy resin and a novolac cresol mold epoxy resin, it is more desirable that they are 400 or less mmols.

[0027] A part of propargyl radical in the resin constituent contained in the cation electroplating paint constituent of this invention may be acetylide-ized. An acetylide is the metal acetylide of salt recombination. As for the content of the propargyl radical in the above-mentioned resin constituent acetylide-ized, it is desirable that they are per [0.1] 100g of resin constituent solid content ~ 40mmol. Acetylide-izing is difficult, if the effectiveness according that they are less than 0.1 mmols to acetylide-izing is not demonstrated enough but exceeds 40mmol. This content can set up the more desirable range according to the metal to be used.

[0028] Especially if it is the metal which demonstrates a catalytic as a metal contained in the propargyl radical acetylide-ized (above), it will not be linked, for example, transition metals, such as copper, silver, and barium, can be mentioned. If environmental compatibility is taken into consideration, copper and silver will be desirable and acetylation use to copper will be [among these] more desirable. When using copper, as for the content of the propargyl radical in the above-mentioned resin constituent acetylide-ized, it is more desirable that they are per [0.1] 100g of resin solid content in the cation electroplating paint constituent of this invention ~ 20mmol.

[0029] By acetylide-izing a part of propargyl radical in the resin constituent contained in the cation electroplating paint constituent of this invention, a curing catalyst can be introduced into resin. Since it can acetylide-ize easily and can introduce even if it generally is not necessary to use the organic transition metal complex which dissolves or is hard to distribute for an organic solvent or water and is transition metals if it does in this way, even if it is a poorly soluble transition-metal compound, it is freely usable to a coating constituent. Moreover, it is valuable for [in the case of using a transition-metal organic-salt salt] that an organic-salt salt exists during electroplated bath as an anion. Further, a metal ion is not removed by ultraviolet and the design of control of bath or a cation electroplating paint becomes easy.

[0030] The resin constituent contained in the cation electroplating paint constituent of this invention may be made to contain a carbon-carbon double bond by request. Since reactivity is high, the above-mentioned carbon-carbon double bond can raise hardenability further.

[0031] The content of the above-mentioned carbon-carbon double bond has per [10] 100g of resin solid content in the cation electroplating paint constituent of this invention ~ desirable 495mmol, after fulfilling the conditions of the content of the propargyl radical mentioned later and a carbon-carbon double bond. When sufficient hardenability cannot be demonstrated by acetylide-izing they are 10mmol(A) / less than 100g, but it exceeds 495mmol / 100g, there is a possibility of having a bad influence on the hydration stability at the time of using it as a cation electroplating paint. When considering of resin with which a more desirable content can be set up according to the resin frame used, for example, the above-mentioned resin constituent makes

a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, as for the content of the above-mentioned carbon-carbon double bond, it is more desirable that it is 20-70mmol.

[0032] When the resin constituent contained in the cation electrodeposition paint constituent of this invention contains the above-mentioned carbon-carbon double bond, as for the sum total content of the above-mentioned propargyl radical and a carbon-carbon double bond, it is desirable that it is within the limits of 100 to 100g of resin solid content in the cation electrodeposition paint constituent of this invention. If there is a possibility that hardenability may become less than 80 mmol inadequate and 450mmol is excessive, the content of a sulfonium radical will decrease, and there is a possibility that throwing power of electrolytic coloring may become inadequate. When the resin constituent which can act up a more desirable content according to the resin frame used, for example, is contained in the above-mentioned cation electrodeposition paint constituent consists of resin which makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, as for the sum total content of the above-mentioned propargyl radical and a carbon-carbon double bond, it is more desirable that it is 100-350mmol.

[0037] When the resin constituent contained in the cation electrodeposition paint constituent of this invention contains the above-mentioned carbon-carbon double bond, as for the sum total content of an above-mentioned sulfonium radical, propargyl radical, and carbon-carbon double bond, it is desirable that they are 500 or less mmol per 100g of resin solid content in the above-mentioned cation electrodeposition paint constituent. If 500mmol or less are exceeded, resin may not be obtained in fact or the target engine performance may not be obtained. When consisting of resin with which a more desirable content can be set up, for example, the above-mentioned resin constituent makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin according to the resin frame used, as for the sum total content of an above-mentioned sulfonium radical, propargyl radical, and carbon-carbon double bond, it is more desirable that they are 400 or less mmol.

[0038] The resin constituent contained in the cation electrodeposition paint constituent of this invention is, for example, the epoxy resin which has at least two epoxy groups in a molecule (A) which has an epoxy group, the functional group which reacts, and a propargyl radical is made to react the process (2) which obtains an epoxy resin constituent with a propargyl radical and a sulfide / acid mixture can be made to be able to react to the residual epoxy group in an epoxy resin constituent with the propargyl radical obtained at the process (3), and it can manufacture suitably according to the process (3) which introduces a sulfonium radical.

[0039] When it is necessary to use together the compound (B) which has an epoxy group, the functional group which reacts, and a carbon-carbon double bond with the above-mentioned compound (A) in the above-mentioned process (3), in giving a carbon-carbon double bond to the resin constituent contained in the cation electrodeposition paint constituent of this invention it is needed.

[0040] When acetylide-izing a part of propargyl radical which the resin constituent contained in the cation electrodeposition paint constituent of this invention has, metallic compounds, such as a complex of transition metals, such as copper, silver, or bromine, or a salt, can be made to be able to react to an epoxy resin constituent with the propargyl radical obtained at the above-mentioned process (3), and the process which acetylide-izes some propargyl radicals in the above-mentioned epoxy resin constituent can be given. The resin constituent contained in the cation electrodeposition paint constituent of above-mentioned this invention can be obtained according to the manufacture approach of a publication to JP.2000-188891A etc.

[0041] In the cation electrodeposition paint constituent of this invention, since the resin constituents which has a sulfonium radical and a propargyl radical as mentioned above is contained and the above-mentioned resin constituent itself has hardenability, use of a curing agent is necessarily unnecessary. However, you may use it in order to raise hardenability further. As such a curing agent, the compound which was made to carry out the addition reaction of the compound which has carbon-carbon double bonds which have propargyl radicals, such as

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propargyl alcohol, such as a compound and an acrylic acid, and obtained it can be mentioned to poly epoxide, such as the compound which has two or more at least one sort in a propargyl radical and carbon-carbon double bond, for example, a novolak phenol etc. per TAERA etc. isocyanate, etc., for example.

[0042] It is not necessary to necessarily use a curing catalyst for the cation electrodeposition paint constituent of this invention. However, when it is necessary to raise hardenability further by the hardening reaction condition, the transition-metal compound usually used may be added suitably if needed. What it was not limited especially as such a compound, for example, carbonyl oxides, such as ligands, such as a cyclohexanone and an acetylacetone, and an azobis, etc. combined to transition metals, such as nickel, cobalt, manganese, palladium, and a rhodium, can be mentioned. As for the loadings of the above-mentioned curing catalyst, it is desirable that it is 0.1-20 % of the weight to the resin solid content weight in the above-mentioned cation electrodeposition paint constituent.

[0043] An amine can be blended with the cation electrodeposition paint constituent of this invention. By combination of the above-mentioned amine, the conversion rate to the sulfide of the sulfonium radical by the electrocatalytic reduction in an electrodeposition process increases. It is not limited especially as the above-mentioned amine, for example, amine compounds, such as fatty amine of monofunctional (of the class 1st / 2nd / 3rd class) and many organo functions, an allyloxy group amine, and aromatic amine, can be mentioned. Among those, a water-soluble or water-dispersible thing is desirable, for example, can mention the alkyllamine monothiolamine of the carbon numbers 2-8, such as monomethylamine, dimethylamine, trimethylamine, triethylamine, propylamine, diisopropylamine, and triethylamine, a diethanolamine, a methylalcohol amine, dimethylmethanolamine, cyclohexylamine, a morpholine, N-methyl morpholine, a pyridine, pyrazine, a piperidine, imidazole, an imidazole, etc. These may be used independently and may use two or more sorts together. Since moisture proof stability is excellent especially, hydroxy amine, such as monothiolamine, diethanolamine, and dimethylmethanolamine, are desirable.

[0044] The above-mentioned amine can be directly blended into the cation electrodeposition paint constituent of this invention. Although the neutralization acid in resin will be taken and the stability of an electrodeposition solution will get worse remarkably in the cation electrodeposition paint of the conventional neutralization acid amine system if the amine of isolation is added, inhibition of such both stability does not arise in this invention.

[0045] The loadings of the above-mentioned amine have per 100g of resin solid content in the cation electrodeposition paint constituent of this invention, and desirable 0.3-25mmol. If sufficient effectiveness cannot be acquired to through 100g of electrolytic coloring as they are 0.3mmol (at / less than 100g, but it exceeds 25mmol / 100g, effectiveness according to an addition amine) be acquired but it is uneconomical. They are 1-15mmol / 100g more preferably.

[0046] The cation electrodeposition paint constituent of this invention may contain further the other components used for the usual cation electrodeposition paint if needed. It is not limited especially as the above and other components, for example, additives for curing, such as a pigment, a rust-proofer, pigment-content powder resin, a surfactant, an anticorrosive, and an ultraviolet ray absorber, etc. can be mentioned.

[0047] What is not limited especially as the above-mentioned pigment, for example, it is used for a cation electrodeposition paint generally (extenders, such as rust preventive pigment; kaolin, such as color pigments; silico-acid lead, such as a titanium dioxide, carbon black, and red ochre; and molybdophosphate acid aluminum, clay, and talc, etc.) can be mentioned. Specifically as the above-mentioned rust-proofer, phosphorous acid calcium, phosphorous acid zinc calcium, a calcium support silicon, a calcium support zeolite, etc. can be mentioned. As for the sum total loadings of the above-mentioned pigment, it is desirable that it is 0-50 % of the weight as solid content in the cation electrodeposition paint constituent of this invention.

[0048] The above-mentioned pigment-content powder resin is used in order to stabilize and distribute the above-mentioned pigment in a cation electrodeposition paint. Especially as pigment-content powder resin, it is not limited and the pigment-content powder resin currently generally used can be used. Moreover, the pigment-content powder resin containing a sulfonium

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radical and an unsaturated bond may be used into resin. The pigment-content powder resin containing such a sulfonium radical and an unsaturated bond can be obtained by the approach of making a sulfide compound reacting to the hydrophobic epoxy resin which for example, a bisphenol mold epoxy resin and half black-ized isocyanate are made reacting, and it is obtained, or making a sulfide compound reacting to the above-mentioned resin under existence of a monobasic acid and a hydroxy-group content diisopropyl acid etc. The above-mentioned pigment-content powder resin can be made to also stabilize and distribute the above-mentioned non-heavy-metal rust-proofer in a cation electrodeposition paint.

[0049] To the above-mentioned resin constituent contained in this, if needed, the cation electrodeposition paint constituent of this invention can mix such above-mentioned components, and can obtain it by dissolving or distributing in water etc. An above-mentioned photopolymerization initiator may be blended by preceeding preparing the above-mentioned cation electrodeposition paint constituent, and distributing the above-mentioned resin constituent, and after sealing in addition to above-mentioned pigment-content powder resin, it may be blended by adding the parts obtained after the time of manufacture of the above-mentioned coating constituent or manufacture. As for the above-mentioned cation electrodeposition paint constituent, it is desirable to adjust so that it may not deviate from the range of above-mentioned (the content of the propargyl radical in the resin constituent contained in this, a carbon-carbon double bond, and a sulfonium radical). In case it uses for cation electrodeposition, as for the above-mentioned cation electrodeposition paint constituent, it is desirable to be prepared so that a nonvolatile matter may serve as 10-30% of both liquid.

[0040] The paint film formation approach of paint film formation approach this invention carries out electrodeposition of the above-mentioned cation electrodeposition paint constituent to a coated object, and includes the process which performs an optical exposure in the coat obtained. The paint film formation approach of this invention may include the process which heats further the coat obtained by electrodeposition. If it does not deteriorate by not being limited and carrying out cation electrodeposition especially as a coated object used for the paint film formation approach of this invention, when it will not be limited but will heat especially, it is still more desirable that it is what does not deteriorate with heating. As such a coated object, what carried out surface treatment of plates, such as a gride, a steel plate, and aluminum, molding, and them can be mentioned, for example.

[0041] The above-mentioned electroplating uses a coated object as cathode, between anode plates, impresses the electrical potential difference of 50-450V, and usually performs it. If it becomes being less than 50V, electrodeposition applied voltage inadequate and it exceeds 450V, power consumption becomes large and it is uneconomical. A uniform coat can be formed in the whole coated object, without producing the rapid rise of thickness in an electrodeposition process, if it is within the limits and an electrical potential difference is impressed (above-mentioned) using an above-mentioned cation electrodeposition paint constituent. The bath liquid temperature of the above-mentioned cation electrodeposition paint constituent in the case of increasing the above-mentioned electrical potential differences usually has desirable 10-45 degrees C.

[0042] The process to which the electric resistance value per unit volume of the above-mentioned coat is made to increase by the above-mentioned electrodeposition's using as cathode the process and the above-mentioned coated object which are immersed in the above-mentioned cation electrodeposition paint constituent in a coated object, impressing an electrical potential difference between anode plates, and impressing an electrical potential difference to the process in which a coat is deposited, and the deposited above-mentioned coat, further -- difference -- being constituted is desirable. Although the above-mentioned electrical-potential-difference impression this amount changes with electrodeposition conditions, generally it can be made into 2-4 minutes. Thus, after termination of an electrodeposition process, cation electrodeposition the non-hardened coat obtained is set, remaining as it is or after rinsing.

[0043] Subsequently the above-mentioned coat non-hardened (electrodeposited) as a polymerization by optical exposure, and is hardened. As the above-mentioned optical exposure, the point of hardenability and variability to UV irradiation is desirable. Although hardening

progresses so that there are generally many exposures, 200-3000 mJ/cm<sup>2</sup> is desirable. If hardening may become being less than 200 mJ/cm<sup>2</sup> inadequate and 5000 mJ/cm<sup>2</sup> is excessive, whenever [hardening] may not increase considering an exposure but it may become uneconomical. It is 900-3000 mJ/cm<sup>2</sup> more preferably.

[0044] Obviously the above-mentioned exposure is expressed by the degree time. [Exposure (mJ/cm<sup>2</sup>) = [Exposure on the strength (mW/cm<sup>2</sup>)] × [Irradiation time (s)] Therefore, the case where can determine the above-mentioned exposure by choosing exposure reinforcement and irradiation time suitably, for example, it irradiates for 0.2-20 minutes by the exposure reinforcement 30-1200 mJ/cm<sup>2</sup> is mentioned.

[0045] It is not limited especially as the approach of the above-mentioned optical exposure, for example, a well-known approach can be used conventionally. When the above-mentioned optical exposure is UV irradiation, a high pressure mercury vapor lamp, a chemical lamp, etc. can be chosen suitably, corresponding to hardening conditions, such as exposure reinforcement and irradiation time. For example, since exposure reinforcement is 1.0-20 mJ/cm<sup>2</sup> is, as for irradiation time, for 1-20 minutes is usually desirable (since peak wavelength is 200-400nm and exposure reinforcement is usually 200-1000 mJ/cm<sup>2</sup> is) when using a high pressure mercury vapor lamp, as for irradiation time for 0.2-10 minutes is desirable, and ], when using a chemical lamp.

[0046] Not only the above-mentioned optical exposure but the process to heat may be given to the coat obtained by the above-mentioned electroplating non-hardened (electrodeposited). As heating conditions, the obtained coated object is thrown into the drying furnace set as 120-240 degrees C, and heating for 5-60 minutes is mentioned to it, for example, in this invention, since the photopolymerization initiator contains in the cation electrodeposition paint constituent and hardening by photopolymerization is performed, it is sufficient to be able to make it harden in low temperature and a short time rather than the heat hardening of the conventional electrodeposited coat, for example, to heat for 10-45 minutes at 120-210 degrees C preferably, and it is sufficient to heat for 10-30 minutes at 130-180 degrees C more preferably.

[0047] When heating a coat in the paint film formation approach of this invention, as for whenever [above-mentioned heating temperature], it is desirable to set it as temperature higher 1-15 degrees C than the curing temperature of an above-mentioned cation electrodeposition paint constituent, and, as for the curing temperature of the above-mentioned cation electrodeposition paint constituent, it is desirable to be set as 130-220 degrees C. When curing temperature is low temperature from 130 degrees C, there is a possibility that the smooth nature of the paint film obtained may fall. There is a possibility that the appearance of the multilayer paint film obtained when the physical properties of the paint film obtained fall when curing temperature is an elevated temperature from 220 degrees C, or painting too coat etc. to it may fall. A setup of the above-mentioned curing temperature can be given to this connector called adjustment of the class of a hardening functional group, a curing agent, and catalyst, an amine, etc. by the well-known approach.

[0048] The curing temperature in this invention means the temperature for obtaining the paint film of 85% of gel molar fractions with heating for 25 minutes. Measurement of the above-mentioned gel molar fraction is performed by the approach of computing from the weight difference of the coat before and behind a trial at the time of being immersed in an acetone and making a test coat and flow back for 5 hours.

[0049] When heating the above-mentioned coat non-hardened (electrodeposited) in the paint film formation approach of this invention, the above-mentioned heating is separately UV the optical exposure of the above-mentioned coat non-hardened (electrodeposited) good in a line. In this case, since an above-mentioned photopolymerization initiator is used in this invention, in order to operate this effectively, after performing the above-mentioned optical exposure, it is desirable to perform the above-mentioned heating.

[0050] As for the paint film formation approach of this invention, it is desirable to include the process which performs the above-mentioned heating and the above-mentioned optical exposure to coincidence to the above-mentioned coat non-hardened (electrodeposited). When the process which performs the above-mentioned heating and the above-mentioned optical

exposure to coincidence is included in all or a part of time amount which performs the above-mentioned optical exposure, the above-mentioned heating can be performed to coincidence. For example, although the process which performs only the above-mentioned heating other than the process which performs the above-mentioned heating and the above-mentioned optical exposure to coincidence, and/or the process which performs only the above-mentioned optical exposure to coincidence, it is desirable to perform the above-mentioned heating to coincidence from the point of hardenability in all of time amount that perform the above-mentioned optical exposure. Adjustment of the time amount which performs the above-mentioned optical exposure can be performed by, for example, adjusting the reinforcement of an optical exposure suitably as mentioned above.

[0051] In the cation electropainting approach of this invention, on the electrodeposited coat obtained by cation electropainting, if needed, in order to give substrate concealment nature and chip-proof nature, an intermediate coat may be applied, and two coats of top coat may be further given for coloring, the improvement in appearance, etc. It is desirable to make it harder before spreading of an intermediate coat, since hardening according to this invention and / or the above-mentioned electrodeposited coat to an optical exposure at least is made to perform.

[0052] Since the cation electrodeposition paint constituent of this invention contains a resin constituent with a sulfonium radical and a propargyl radical, the electrodeposited paint film excellent in throwing power of electrolytic coloring is obtained. Coat hardening by photopolymerization which did not have the cation electrodeposition paint constituent of this invention in conventional automobile car body and electrodeposition paint for components since the radical occurred by the sulfonium radical, it acted on the partial saturation double bond in which the above-mentioned radical is contained by a propargyl radical and the case and the polymerization reaction advanced when the optical exposure was performed to the non-hardened electrodeposition coat obtained by electropainting, since an above-mentioned photopolymerization initiator is included again is realized. Thereby, compared with the conventional heat hardening, hardening in low temperature and a short time is attained, and advantageous effectiveness, such as expansion of the selection width of face of the electropainting and the hardening conditions of being able to adopt a photopolymerization hardening system besides the weatherproof improvement, not only in the cost reduction by energy saving and short-time-ting but the hardening cost obtained, a low thermal-resistance base material, and cold cure, is acquired. By performing optical exposure and heating to coincidence, the above-mentioned hardening can improve further and can attain further low-temperature-izing and short-time-izing of hardening. Therefore, the coated object which has the coat obtained by the paint film formation approach and the above-mentioned paint film formation approach using the cation electrodeposition paint constituent of this invention and the above-mentioned cation electrodeposition paint constituent is used especially suitable for electropainting, such as a car body of an automobile, and components.

[0053]

[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples. Example 1 of manufacture in addition to the flask equipped with an agitator, a thermometer, nitrogen installation tubing, and a reflux cooling pipe, carried out the temperature up of propargyl alcohol 30.6g and the dimethyl benzylamine 0.2g to 125 degrees C, it was made to react to 100.0g (EPO TOTO YD0N-701, Tohda Kasei Co., Ltd. make) of  $\alpha$ -methyl novolak mold epoxy resins of this manufacture weight per epoxy equivalent 200.4 of an epoxy resin constituent with a sulfonium radical and a propargyl radical for 5 hours, and the resin which has the propargyl radical of weight per epoxy equivalent 1800 was obtained. Furthermore, 100.0g of this reactant was divided to the flask equipped with an agitator, a thermometer, nitrogen installation tubing, and a reflux cooling pipe, 1-(2-hydroxyethyl)thio-2 and 3-propanediol 0.0g, 3.0g of glacial acetic acid, and 8.4g of deionized water were put in, the temperature up was carried out to 75 degrees C, and it was made to react for 6 hours. It checked that the residual acid number was smaller than 5, 28.8g of deionized water was added further, and the target resin solution was obtained.

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Solid content concentration was 70.0 % of the weight, and number average molecular weight was 3100.

[0054] The water paint liquid whose solid content concentration is once 50% was prepared having added deionized water to the resin solution obtained in the example 1 of example 1 (manufacture of cation electrodeposition paint constituent) manufacture gradually, and fully stirring by DISLUPA. To this, 3 % of the weight and pure water were added for benzyl dimethyl xetal (USJGAKYUA TR8931, Ciba-Gelby make) to resin solid content weight as a photopolymerization initiator, and the cation electrodeposition paint constituent whose solid content concentration is 15% was obtained. When the curing temperature of this cation electrodeposition paint constituent was measured, it was 180 degrees C.

[0055] (The cation electropainting approach) The obtained cation electrodeposition paint constituent was moved to the stainless steel container, and it considered on the electrodeposited bath, and electropainting was performed so that it might become 15 micrometers of deposition thickness on a coated object here, as the cold rolled steel plate (phosphoric-acid zinc processing agent surfboard dyne by Nippon Paint Co., Ltd. JIS G3141 SPCC-SD, SD= 5000 processing) having carried out phosphoric-acid zinc processing served as cathode. With the condition of having raised the coated object pulled up from the electrodeposited bath after electropainting and in a stainless steel container on the oil level, it rinses, after making it a cation naturally for 30 seconds, and it is a high pressure mercury vapor lamp (the peak wavelength of 254nm). After performing UV irradiation for 1 minute using exposure on the strength 500 mJ/cm<sup>2</sup>-m<sup>-1</sup> and the OAK CO., LTD. make, the color card was created by heating for 25 minutes at which [ 150 degrees C, 180 degrees C, 170 degrees C, 160 degrees C, 150 degrees C, and 200 degrees C ] temperature.

[0056] (Evaluation of hardenability) The paint plate which carried out in this way and was created was put into the Soxhlet extractor, it extracted under the reflux condition for 8 hours using the mixed liquor of an acetone / methanol =1/1, and the gel molar fraction of the hardening paint film was computed according to the degree type, a gel molar fraction = ( % ) extract Shigakazu Ushiro / extract Saki [ Shigakazu ] (g) x100 result was shown in Table 1.

[0057] Performing example 2 UV irradiation for 25 minutes using the chemical lamp (JE-A2, exposure reinforcement of 5.6mW, the JEOL energy machine company make), everything but heating for 25 minutes to this and coincidence created and evaluated the color card like the example 1. In addition, the amount of UV irradiation is the same as an example 1. A result is shown in Table 1.

Everything but heating for 25 minutes created and evaluated the color card like the example 1, without performing example UV irradiation of reference. A result is shown in Table 1

[0058]

Table 1

照射条件	抽出液の抽出率(%)					
	150℃	160℃	170℃	180℃	190℃	200℃
例1 (UV照射25分)	98	99	99	99	99	99
例2 (UV照射25分)	97	99	99	99	99	99
例3 (加熱25分)	99	99	99	99	99	99

[0059] Although it was inferior to hardenability from Table 1 in the example of reference which does not perform UV irradiation since the gel molar fraction was low, in the example 1 which performs UV irradiation apart from heating, hardenability improved and it turned out that hardenability is further excellent in the example 2 which performs UV irradiation to heating and coincidence.

[0060]

(Effect of the invention) Since the cation electrodeposition paint constituent of this invention consists of an above-mentioned configuration, photopolymerization can be made to perform paint film hardening after cation electropainting, and cold cure and short-time hardening are realized. Since the paint film formation approach of this invention performs an optical exposure,

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the cold cure of it may become possible, and heating may be used together, by performing heating to an optical exposure and coincidence, hardenability improves and cold cure and short-time hardening are promoted further. Therefore, the coated object which has the coat obtained by the cation electrodeposition paint constituent, the paint film formation approach, and the above-mentioned approach of this invention is used suitable for point of the car body of an automobile, or components.

[Translation done]